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CONTRACT N00014-95-1-0028

R&T Code 4131D02

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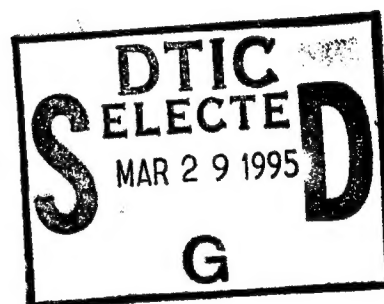
Technical Report No. 79

COMPUTATIONAL INVESTIGATION OF THE STABILITIES  
OF SOME N, O, F IONS

by

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March 16, 1995

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DTIC QUALITY INSPECTED 1

19950327 156

## REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

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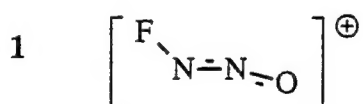
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE March 16, 1995		3. REPORT TYPE AND DATES COVERED Technical Report	
4. TITLE AND SUBTITLE Computational Investigation of the Stabilities of Some N, O, F Ions				5. FUNDING NUMBERS N00014-95-I-0028  Dr. Richard S. Miller  R&T Code 4131D02	
6. AUTHOR(S) M. Edward Grice and Peter Politzer					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of New Orleans Department of Chemistry New Orleans, Louisiana 70148				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Code 333 800 N. Quincy Street Arlington, VA 22217				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES  By _____ Distribution / _____  Availability Codes Dist Avail and/or Special A-1				Accession For NTIS CRA&I <input checked="" type="checkbox"/> DTIC TAB <input type="checkbox"/> Unannounced <input type="checkbox"/> Justification _____	
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release. Unlimited distribution				12b. DISTRIBUTION CODE "	
13. ABSTRACT (Maximum 200 words)  In response to the suggestion of Jeff Bottaro (SRI International), we have investigated the potential stabilities of four N, O, F ions, 1 - 4. All four molecular geometries were optimized using a non-local density functional (DF) procedure (Gaussian 92/DFT; BLYP/6-31+G**) and also at the <i>ab initio</i> MP2/6-31+G** (frozen core) level. For 1, the MP optimization was carried out as well without the frozen-core approximation. All calculations were for spin-restricted singlet states; however the DF results were checked for stability relative to allowing them to become spin-unrestricted and/or complex and were determined to be stable in this respect. In order to ascertain whether the optimized structures correspond to true energy minima, vibration frequencies were computed for all four systems at the DF level and for 1 and 2 at the MP2; for the anions 3 and 4, the number of basis functions being used precluded MP2 frequency calculations. No imaginary vibration frequencies were found. This confirms that the optimized structures of all four systems do correspond to true energy minima, and that these ions should be able to exist.					
14. SUBJECT TERMS N, O, F ions; density functional calculations; stabilities				15. NUMBER OF PAGES 3	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited		

In response to the suggestion of Jeff Bottaro (SRI International), we have investigated the potential stabilities of four N, O, F ions, 1 - 4.

All four molecular geometries were optimized using a non-local density functional (DF) procedure (Gaussian 92/DFT; BLYP/6-31+G\*\*) and also at the *ab initio* MP2/6-31+G\*\* (frozen core) level. For 1, the MP optimization was carried out as well without the frozen-core approximation. All calculations were for spin-restricted singlet states; however the DF results were checked for stability relative to allowing them to become spin-unrestricted and/or complex and were determined to be stable in this respect.

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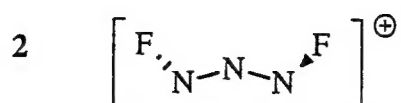
The computed energies and geometries are shown below. Energies are in hartrees (1 hartree = 627.5 kcal/mole), distances in Å and angles in degrees. For the most part, the geometries obtained by the two procedures are very similar.



Both DF and MP2 optimizations gave a planar C<sub>s</sub> structure.

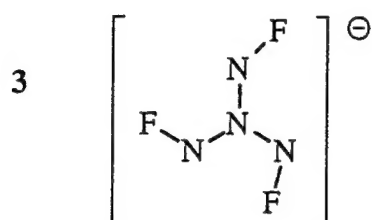
	DF	MP2-FC	MP2
Energy	-283.99968	-283.30446	-283.31763
F-N	1.343	1.335	1.333
N-N	1.216	1.208	1.204
O-N	1.164	1.155	1.155
F-N-N	121.80	126.96	126.51
O-N-N	157.98	157.91	158.28

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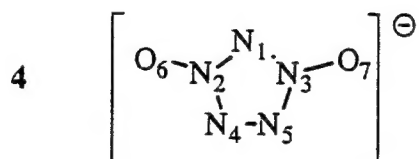
Both optimizations gave a  $C_2$  structure with bent N-N-N and the fluorines out of the N-N-N plane.

	DF	MP2-FC
Energy	-363.33081	-362.43088
F-N	1.361	1.348
N-N	1.241	1.233
F-N-N	112.14	110.38
N-N-N	147.94	156.18
F-N-N-N	135.9	135.2



The DF optimization gave a planar  $C_{3h}$  structure. The MP2 optimization was constrained to  $C_{3h}$ .

	DF	MP2-FC
Energy	-518.28869	-517.01888
F-N	1.502	1.461
N-N	1.363	1.347
F-N-N	104.04	103.68



The DF optimization gave a planar  $C_{2v}$  structure. The MP2 optimization was constrained to  $C_{2v}$ .

	DF	MP2-FC
Energy	-424.07269	-423.02031
N1-N2	1.373	1.361
N2-N4	1.361	1.357
N4-N5	1.351	1.345
N-O	1.281	1.266
N2-N1-N3	101.72	101.83
N4-N2-N1	112.52	112.66
N5-N4-N2	106.62	106.42
O6-N2-N4	124.30	124.24
O6-N2-N1	123.18	123.10